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1575 W. Hunt Highway, Florence, Arizona 85132 USA

florence copper com-

September 18, 2018

Mr. David Albright U.S. Environmental Protection Agency Region 9, Ground Water Office, WTR-9 75 Hawthorne Street San Francisco, California 94105-3901

Re: Transmittal of Proposed Procedures for Determining Alert Levels and Aquifer Quality Limits for Groundwater Compliance Monitoring, Florence Copper Project

Dear Mr. Albright:

Florence Copper, Inc. (Florence Copper) herewith transmits the enclosed *Proposed Procedures for Determining Alert Levels and Aquifer Quality Limits for Groundwater Compliance Monitoring, Florence Copper Project* for review by the U.S. Environmental Protection Agency. This submittal presents a proposed method for establishing Alert Levels and Aquifer Quality Limits in cases where the standard methodology may provide sufficient protection against false positive indications.

Florence Copper looks forward to your review and to discuss contents of this submittal with your team and value your input regarding the proposed methods. This submittal was prepared to satisfy the requirements of Part II.F.2 and 3 of the Underground Injection Control Permit R9UIC-AZ3-FY11-1.

Please contact me at 520-374-3984 if you or your team requires any additional information.

Sincerely,

Florence Copper Inc.

Daniel Johnson

Vice President - General Manager

cc:

Nancy Rumrill, U.S. Environmental Protection Agency

Maribeth Greenslade, Arizona Department of Environmental Quality

Attachment:

Proposed Procedures for Determining Alert Levels and Aquifer Quality Limits for Groundwater Compliance Monitoring

# Proposed Procedures for Determining Alert Levels and Aquifer Quality Limits for Groundwater Compliance Monitoring

Florence Copper Project Florence, Arizona

April 25, 2018



### INTRODUCTION

Temporary APP No. P-106360 requires the calculation of alert levels (ALs) and aquifer quality limits (AQLs) for groundwater compliance monitoring at the Florence Copper Inc. facility (Facility).

The permit outlines methodology for calculating ALs, along with a set of criteria to follow for selecting the final AL and AQL in Permit Conditions 2.5.3.2.1 – Alert Levels for POC Wells, and 2.5.8.5.1 – Alert Levels for Supplemental Wells and MW-01. Based on preliminary evaluation of the data, the majority of the ALs can be set using the permit-described methodology. In cases where datasets have reduced variability, this document outlines proposed modifications to the permit method.

Please note that some example datasets are provided for the purposes of demonstration and are not considered to be complete or final.

# PERMIT METHODOLOGY

The Temporary Aquifer Protection Permit (APP) outlines the methodology for setting ALs and AQL. There are three general steps:

- Data preparation;
- Using the mean and standard deviation to calculate a statistical AL; and
- · Using case criteria to determine the final ALs and AQLs.

# DATA PREPARATION

#### Permit Methodology

Data will be prepared for AL calculations as outlined in the Temporary APP.

- ALs will be calculated using a minimum of 8 and a maximum of 12 consecutive sample rounds.
  - o In the majority of cases, 9 sample results will be used; except where an outlier is identified.
- Any data where the laboratory practical quantitation limit (PQL) exceeds 80% of the AWQS will be excluded from the calculations.
- Obvious outliers will be excluded from the calculations.
  - o Outliers will be determined primarily on the basis of graphical review.

In addition, it is proposed that:

Duplicate analytical results will be removed.

## **Handling of Non-Detect Values**

The APP prescribes using a value of one-half of the PQL for results below the detection limit for the calculation of ALs. This is used where greater than 50% of the results are non-detect.



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For cases where a dataset contains at least one non-detect but less than 50% of the results are non-detect, the statistical method proposed below accommodates the non-detects, which only need to be identified at the value of the PQL.

# ALERT LEVEL CALCULATIONS

# **Permit Methodology**

The permit prescribes calculation of the ALs based on a tolerance interval. The AL is calculated with the following equation:

$$AL = \bar{x} + k \cdot s$$

where:

 $\bar{x}$  = the mean of the existing concentrations in a given well;

s = the standard deviation of the existing concentrations in a given well; and

k = a multiplicative factor that accounts for uncertainty in the analysis and the desired coverage and confidence of the AL (discussed below)

The values of  $\bar{x}$  and s are calculated from the existing concentrations using appropriate statistical methods.

# Development of the k Constant

The permit recommends using the Lieberman Tables for a one-side normal tolerance interval with a 95% confidence level. Based on a 99% coverage and a sample size of 9, the k value for this data set would be 4.143.

In reviewing preliminary calculations, it was observed that many of the datasets have low-variability, resulting in ALs that only marginally exceed the maximum observed value. Table 1A — Example Case 1 shows the calculation of the AL for a magnesium dataset with no non-detect values:

Average – 9.0

Maximum – 11

Standard Deviation – 1.2

Calculated UPL = 9.0 + 1.2 \* 4.143 = 14

Because the AL is only marginally higher than the maximum observed value, it is likely that a result may exceed the calculated AL due to natural water quality variation. The 99% coverage of the AL means that the AL represents the 99th percentile of the dataset, which would be exceeded approximately 1% of the time even under natural conditions. Based on the number of wells and analysis required for the project, this could translate to as many as 10 false positives in a year.



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# Modified k Value - Upper Prediction Limit

An alternative statistical method for calculating the k value is described by the United States Environmental Protection Agency (EPA) in "Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities — Unified Guidance" (EPA, 2009). The AL calculated is an Upper Prediction Limit (UPL), representing a value that is unlikely to be exceeded by any single future measurement, unless groundwater conditions have changed. The value of k is calculated as:

$$k = t_{1-\infty,n-1} \cdot \sqrt{1 + \frac{1}{n}}$$

where:

n = the sample size of the existing concentration dataset for a given well;

 $t_{1-\infty,n-1}$  = the value of the t-distribution for the given values of n and  $\propto$ 

Because the dataset of existing concentrations represents only a sample of the full range of possible concentrations, the chance that the UPL will be exceeded even in the absence of a release to groundwater cannot be reduced to zero. The chance that the UPL will be exceed in the absence of a release to groundwater is managed through the chosen value for  $\propto$ .

An exceedance of a UPL even in the absence of a release to groundwater is called a "false positive." The expected rate of occurrence of false positives (i.e., the false positive rate) is controlled through the value of  $\propto$ .  $\propto$  is equal to the desired false positive rate, and thus a value of  $\propto$  = 0.01 would indicate that the UPL has a 1% chance of being exceeded every time a new sample is collected, even if a release to groundwater has not occurred.

Future groundwater samples will be compared to ALs and AQLs for many parameters in many wells multiple times per year. Even if every UPL had only a 1% chance of recording a false positive during each comparison to a new data point, the chance of observing at least one false positive throughout the year would be unacceptably high. To avoid this problem, the false positive rate of each UPL is set at a sufficiently small value to ensure that the overall false positive rate over the course of the year (called the cumulative false positive rate) is reasonably small.

The value of  $\propto$  for each UPL is determined from the desired cumulative false positive rate using the following equation (EPA, 2009):

$$\alpha = 1 - \left(1 - \alpha_C\right)^{1/N_T}$$

where:

 $\propto_C$  = the desired cumulative false positive rate; and

 $N_T$  = the number of tests (i.e., comparisons to a UPL) conducted over the course of a year.

The number of comparisons to a UPL per year is determined from the number of parameters, number of wells, and sampling frequency. For this APP, four parameters (the common ions) are



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sampled four times per year. A full set of parameters (27 parameters in total) is sampled twice per year. The number of wells that are to be sampled each year include the 3 new POC wells, 9 supplemental wells plus 4 existing POC wells that already have established ALs and AQLs. Thus, the total number of comparisons per year is 992.

The cumulative false positive rate is chosen to minimize, to the degree possible, the chances of observing at least one false positive in a given year. The trade-off to choosing a low cumulative false positive rate is that the value of k, and thus the UPLs, increase and are less sensitive to detecting releases to groundwater. However, given the nature of the mining solutions, a release to groundwater would be expected to produce a significant change in groundwater chemistry, quickly exceeding the ALs. Thus, minimizing false positives can be achieved without limiting the effectiveness of the groundwater monitoring program.

The value of the cumulative false positive rate selected in this analysis is 0.01. This means that there will approximately a 1% chance of observing at least one false positive every year, provided that groundwater conditions do not change (either due to a release or through natural variation). In other words, false positives will be expected to occur with a frequency of one every 100 years, assuming stable groundwater conditions.

The cumulative false positive rate of 0.01 gives a value of  $\propto$  for each UPL of 1.01 x 10-5, which gives a value for k of 9.37 when the sample size of the dataset is 9. Although the k value would be higher for any data set with 8 samples, where an outlier is excluded, the same k value of 9.37 will be used for consistency, since this is a more conservative result.

Using this proposed k value for the example case yields a UPL that is less likely to have false positives but is nonetheless protective of groundwater.

For Example Case 1:

Average – 9.0

Maximum – 11

Standard Deviation – 1.2

Calculated UPL = 9.0 + 1.2 \* 9.37 = 20

#### **Adjusted Standard Deviation**

In some cases, the datasets have extremely low variability. This is not unexpected because the data were collected over a relatively short period of time and may not reflect long-term variability in groundwater conditions. Table 1B - Example Case 2 demonstrates the potential for a UPL, using the revised k value, that is still likely to result in false positives:

Average – 23.3

Maximum – 24

Standard Deviation – 0.5

Calculated UPL = 23.3 + 0.5 \* 9.37 = 28

A water-quality variation of less than 15% would yield an exceedance.

To account for the low variability, it is proposed to adjust the standard deviation:



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- The coefficient of variation (CV) will be calculated for each dataset. The CV, which is equal to the standard deviation divided by the mean, is a standardized measure of variability. In other words, the CV for a dataset with a mean of 1,000 can be directly compared with the CV for a dataset with a mean of 10. The same cannot be said for the standard deviation, which is dependent on the magnitude of the data points as well as the variability.
- For datasets with a CV less than 0.1, the standard deviation will be set to 10% of the mean.

## For Example Case 2:

Average - 23.3

Maximum - 24

Standard Deviation - 0.5

Coefficient of Variation = 0.02, below 0.1

Adjusted Standard Deviation = 10% of Average = 2.3

Calculated UPL = 23.3 + 2.3 \* 9.37 = 45

This yields a UPL that is similar in relative magnitude to the dataset as Example Case 1 and less prone to false positives.

#### **Datasets with Non-Detects**

For datasets with all detected results, the mean and standard deviation are calculated using standard methods (e.g., arithmetic average and sample standard deviation formulas found in software such as Microsoft Excel).

If a dataset contains at least one non-detect but the percentage of non-detects is less than 50%, it is proposed to calculate the mean and standard deviation using the Kaplan-Meier Method, as recommended by Helsel (2005). All calculations will be performed in Microsoft Excel, the R Statistical Programming Language (R Core Team, 2016), or the EPA's ProUCL software, version 5.1 (EPA, 2015).

For datasets with 50% or more non-detects, it is proposed to use the permit-described method, substituting non-detect values with one half the value of the PQL to calculate the average and standard deviation of the dataset. If appropriate, an adjusted standard deviation of 10% of the mean would be used.

For datasets with 100% non-detects, it is proposed to use an average of the PQLs and an adjusted standard deviation of 10% of the mean.

Examples of the three types of non-detect datasets are shown in Table 1C — Example Case 3. While these last two approaches are not ideal, they at least provide estimates for UPLs for comparison to a standard, or provide a UPL where no standard exists. Parameters with large numbers of non-detects include certain trace metals, organics, and radium.

# **UPLs by Well vs by Parameter**

Four parameters have been selected in the Temporary APP as primary indicator parameters. Individual UPLs will be calculated for these on a well-by-well basis.



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For metals, organics, and radiochemicals where there is limited variability and large number of non-detects, it is proposed to use the highest UPL calculated for the 12 wells in order to have a standardized AL. However, in the event that a well is significantly different from the other wells, a standard UPL will be set for the main group of wells and a separate UPL for the well(s) with unique results. For example, many total radium values are non-detect; however, two wells have exhibited total radium values above the Aquifer Water Quality Standard (AWQS). In this case, the highest UPL calculated for the first ten wells would be used for those wells, and then a separate UPL calculated for each of the remaining two wells which have values above the AWQS.

# ALS AND AQLS FOR PARAMETERS WITH AWQS

Once a UPL has been calculated, it will be compared to the numerical AWQS to determine the final AL and AQL in accordance with the permit. Table 2 outlines the case criteria described in the permit. Table 3 gives a summary of what method will most likely be used to set the final AL for each parameter; however, this is based on preliminary data and subject to change.

# **Permit Methodology**

Numerical AWQS have been established for fluoride, eleven (11) trace metals, benzene, toluene, ethylbenzene, xylene (BTEX), alpha, and radium. For each parameter with an AWQS, the ALs and AQLs will be set as follows:

#### Case 1 - POC Wells

- If greater than 50% of the results for a well are non-detect, then the AL will be set at 80% of the AWQS and the AQL will be set equal to the AWQS;
- If the calculated UPL is less than 80% of the AWQS, then the AL will be set at 80% of the AWQS and the AQL will be set equal to the AWQS;
- If the calculated UPL is greater than 80% of the AWQS but less than the AWQS, then the AL will be set equal to the UPL and the AQL will be set equal to the AWQS; and
- If the calculated UPL is greater than the AWQS, then the AQL will be set equal to the calculated UPL,
   and no AL will be set for that parameter at that monitoring point.

#### Case 2 - Supplemental Wells

- If greater than 50% of the results for a well are non-detect, then the AL will be set at 80% of the AWQS;
- If the calculated UPL is less than 80% of the AWQS, then the AL will be set at 80% of the AWQS;
- If the calculated UPL is greater than 80% the AWQS but less than the AWQS, then the AL will be set
  equal to the calculated UPL value; and
- · AQLs are not required for supplemental wells.

Note that nitrate has an AWQS; however, the Temporary APP states that ALs and AQLs will not be established for nitrate as it is not a parameter of concern for the process.



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# ALS FOR INDICATOR PARAMETERS

# Indicators with Secondary Standards

Indicator parameters do not have an established AWQS. Secondary drinking water standards (SDWS) are available for sulfate, total dissolved solids (TDS), and five trace metals. For each parameter with an SDWS, it is proposed to set ALs using the same methodology described above.

- If greater than 50% of the results for a well are non-detect, then the AL will be set at 80% of the SDWS:
- If the calculated UPL is less than 80% of the SDWS, then the AL will be set at 80% of the SDWS;
- If the calculated AL is greater than 80% the SDWS, then the AL will be set equal to the calculated UPL value; and
- For the five trace metals, as the concentrations are generally low and the indicator parameters are
  not of primary concern for groundwater protection, the AL will be set equal to the highest AL in any
  well for each indicator metal.

# **Indicators with No Secondary Standard**

Two parameters, magnesium and cobalt, do not have an AWQS or SDWS.

- · The AL for magnesium will be set to the calculated UPL for each well; and
- The AL for cobalt in all wells will be set to the highest calculated UPL for any well.

AQLs are not required for parameters that do not have an established AWQS.

# REFERENCES

- EPA (United States Environmental Protection Agency), 2009. Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities Unified Guidance. Office of Resource Conservation and Recovery. EPA 530/R09-007. March.
- EPA (United States Environmental Protection Agency), 2015. ProUCL Version 5.1.00 Technical Guide Statistical Software for Environmental Applications for Data Sets with and without Nondetect Observations. October.
- Helsel, D. R., 2005. Nondetects and Data Analysis Statistics for Censored Environmental Data. Wiley-Interscience A John Wiley & Sons, Inc., Publication. Hoboken, NJ.
- R Core Team, 2016. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL <a href="https://www.R-project.org/">https://www.R-project.org/</a>.



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TABLE 1A - EXAMPLE CASES DEMONSTRATING PROPOSED UPL CALCULATIONS

	Example С	ase 1			
		Using the Permit <i>k</i> Factor			
	and the Proposed	UPLK Factor.			
M57-O					
Description	Magnesium	Comments			
Results	11	Example Values Detected at Each Sampling			
	7.5	Event			
	7.6				
	10				
	9.4				
	9.0				
	9.0				
	8.6				
Number of Samples	8				
Number of Detections	8				
Number of Non-Detections	0				
Percentage of Non-Detect	0%				
Maximum Value Detected	11				
	Direct				
Calculation Method	Calculation				
Average of Detected Values	9.0				
Standard Deviation	1.2				
Permit k Value	4.143	One-side Tolerance Interval, 95% Confidence			
Calculated AL Using Permit k	13.8	Not Protective Against False Positives			
Proposed k Value	9.37	UPL with 99% Confidence Level			
Revised AL Using Proposed k	20	Sufficiently Protective Against False Positives			

 - 2	(3)	

All results in milligrams per Liter (mg/L). UPL = Upper Prediction Limit

**TABLE 1B - EXAMPLE CASES DEMONSTRATING PROPOSED UPL CALCULATIONS** 

		ase 2 he Traditional Standard Deviation d Standard Deviation
anu tri	M52-UBF	s Standard Deviation
Description	Magnesium	Comments
Results	24	Example Values Detected at Each Sampling
	23	Event
	23	
	23	
	23	
	24	
	23	
	23	
Number of Samples	8	
Number of Detections	8	
Number of Non-Detections	0	
Percentage of Non-Detect	0%	
Maximum Value Detected	24	
	Direct	
Calculation Method	Calculation	
Average of Detected Values	23.3	
Proposed k Value	9.37	UPL with 99% Confidence Level
Standard Deviation	0.5	Traditional Standard Deviation
Calculated UPL	27.6	Not Protective Against False Positives
Coefficient of Variation	0.02	StDev/Ave Must be Greater than 0.1
Adjusted Standard Deviation	2.3	10% of Average
Revised UPL Using Adjusted Standard Deviation	45	Sufficiently Protective Against False Positive

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N,	3.5	<b>5</b> 3	5:

All results in milligrams per Liter (mg/L). UPL = Upper Prediction Limit

TABLE 1C - EXAMPLE CASES DEMONSTRATING PROPOSED UPL CALCULATIONS

		Example Co	ise 3		
Examples of Calculations which Require Handling of Non-Detect Values					
Description	<50% ND M58-O Fluoride	>50% ND M52-UBF Cobalt	100% ND M52-UBF Aluminum	Comments	
Results	0.96	100000	646		
:	0.72	0.00028		Example Values at Each Sampling Event	
	0.57				
	0.68	0.00028			
	0.60				
	0.1	0.000125	0.00		
	0.00	0.000025	0.00		
		0.000125	0.00		
Number of Samples	8	8	8		
Number of Detections	5	2	.0		
Number of Non-Detections	3	6	8		
Percentage of Non-Detect	38%	75%	100%		
Maximum Value Detected	0.96	0.00028	NA		
		Substitute	Stnd Dev-10%		
Method of Handling Non-Detects	Kaplan-Meier	50% PQL	PQL		
Average Value	0,59	0.00016	0.055		
Standard Deviation	0.18	0.00007	<del>~</del>		
Coefficient of Variation	0.31	0.44	•	StDev/Ave Must be Greater than 0.1	
Adjusted Standard Deviation	ж	*	0.006	10% of Average	
Proposed k Value	9.37	9.37	9.37	UPL with 99% Confidence Level	
Calculated UPL	2.32	8000.0	0.11	Sufficienty Protective Against False Positive	

### Notes:

All results in milligrams per Liter (mg/L).
UPL = Upper Prediction Limit

Red = Values are non-detected at the PQL shown.

Italics = Values have been replaced with half the PQL.

TABLE 2 - CASE CRITERIA FOR SETTING ALS AND AQLS

	PARAMETERS WITH AWQS	wester head of his to the colored by	a sassada ha Kiril d
Well Type	Calculated UPL is:	AL	AQL
	> 50% non-detects	80% AWQS	AWQS
Case 1 - POC Wells	< 80% AWQS	80% AWQS	AWQS
Case 1 - POC Wells	Between 80% and AWQS	UPL	AWQS
	> AWQS	UPL	UPL
	Calculated UPL is:	AL	AQL
Case 2 - Supplemental Wells	> 50% non-detects	80% AWQS	None
	< 80% AWQS	80% AWQS	None
	> 80% AWQS	UPL	None
	PARAMETERS WITH SDWS		
Well Type	Calculated UPL is:	AL	AQL
	> 50% non-detects	80% SDWS	None
All Wells	< 80% SDWS	80% SDWS	None
	> 80% SDWS	UPL	None
PARA	METERS WITH NO STANDA	\RDS	
WellType	Calculated UPL is:	AL	AQL
All Wells	UPL	UPL	None

TABLE 3 - ANALYTICAL PARAMETERS REQUIRING AL/AQL CALCULATIONS

A 1	010100	SDWS	AL Method <sup>1</sup>		
Analyte	AWQS Com	mon lons	ALIVIETNOG		
Fluoride	4	2	80% AWQS		
Magnesium	NE	NE	Well by Well		
Sulfate	NE	250	Well by Well		
TDS	NE	500	Well by Well		
	Trac	e Metals			
Aluminum	NE	0.2	80% SDWS		
Antimony	0.006	NE	80% AWQS		
Arsenic <sup>2</sup>	0.01	NE	80% AWQS		
Barium	2	NE	80% AWQS		
Beryllium	0.004	NE	80% AWQS		
Cadmium	0.005	NE	80% AWQS		
Chromium	0.1	NE	80% AWQS		
Cobalt	NE	NE	Highest Calculated AL		
Copper	NE	1	80% SDWS		
Iron	NE	0.3	Highest Calculated AL		
Lead	0.05	NE	80% AWQS		
Manganese	NE	0.05	Highest Calculated AL		
Mercury	0.002	NE	80% AWQS		
Nickel	0.1	NE	Highest Calculated AL		
Selenium	0.05	NE	80% AWQS		
Thallium	0.002	NE	80% AWQS		
Zinc	NE	5	80% SDWS <sup>4</sup>		
Organics					
Benzene	0.005	NE	80% AWQS		
Ethylbenzene	0.7	NE	80% AWQS		
Toluene	1	NE	80% AWQS		
Xylene	10	NE	80% AWQS		
	Radio	chemicals			
Alpha <sup>3</sup>	15	NE	Highest Calculated AL		
Radium 226+228	5	NE	Highest Calculated AL4		

### Notes:

- 1) The Alert Level Method is estimated based on preliminary data and subject to change.
- 2) MCL Value for arsenic is used per the permit.
- 3) The AWQS applies to Adjusted Alpha which equals Gross Alpha minus Uranium Isotopes. Adjusted Alpha is calculated if Gross Alpha is greater than 12 picocuries per liter, otherwise Gross Alpha is used.
- 4) In all cases, if individual well results are significantly different from the average, a separate AL will be set for the well, while the remaining wells may follow the described method.

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